Supporting Information

Grain Boundaries Softening Thermoelectric Oxide BiCuSeO

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Illustration of three GB structures

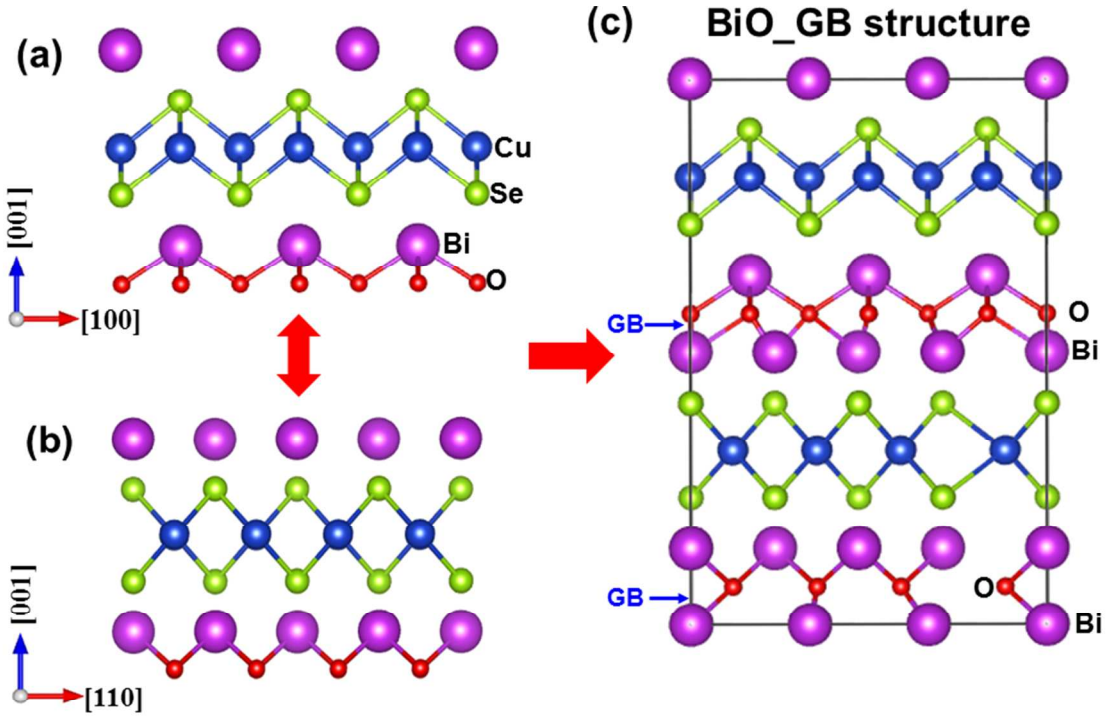

Figure S1. The BiO_GB structure. The BiCuSeO(100) grain with the O atom in the bottom (Figure S1(a)) coheres with the BiCuSeO(110) grain with the Bi atom in the top (Figure S1(b)), which forms the BiCuSeO(100) / BiCuSeO(110) GB (Figure S1(c)). Here, the GB structure couples with the Bi–O bond. Thus, we name this GB as the BiO_GB. The supercell in Figure S1 (a) contains (3×3×1) BiCuSeO(100) oriented unit cell with the lattice parameter $a = b = 11.85$ Å, $c = 9.09$ Å. The supercell in Figure S1 (b) contains (2×2×1) BiCuSeO(110) oriented unit cell with the lattice parameter $a = b = 11.18$ Å, $c = 9.09$ Å. The BiO_GB structure contains 136 atoms. The Bi, Cu, Se, and O atoms are represented with purple, dark-blue, light-green, and red spheres, respectively.

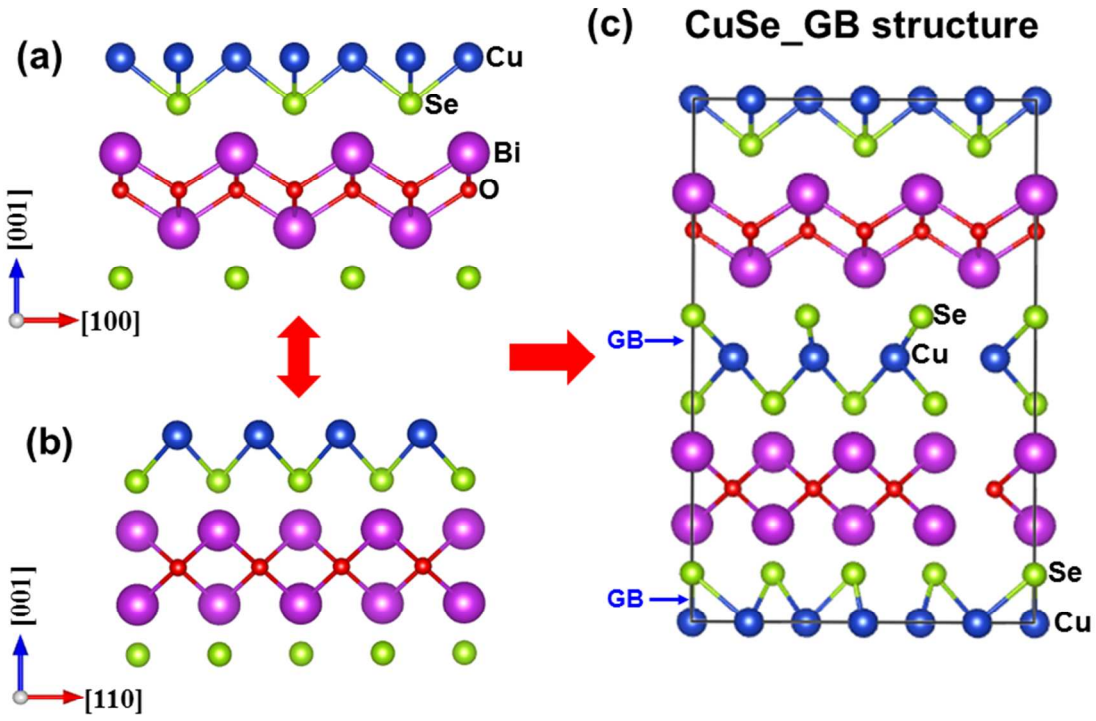

Figure S2. The CuSe_GB structure. The BiCuSeO(100) grain with the Se atom in the bottom (Figure S2(a)) coheres with the BiCuSeO(110) grain with the Cu atom in the top (Figure S2(b)), which forms the BiCuSeO(100) / BiCuSeO(110) GB (Figure S2(c)). Here, the GB structure couples with the Cu-Se bond. Thus, we name this GB as the CuSe_GB. The supercell in Figure S2 (a) contains (3×3×1) BiCuSeO(100) oriented unit cell with the lattice parameter $a = b = 11.85$ Å, $c = 9.09$ Å. The supercell in Figure S2 (b) contains (2×2×1) BiCuSeO(110) oriented unit cell with the lattice parameter $a = b = 11.18$ Å, $c = 9.09$ Å. The CuSe_GB structure contains 136 atoms. The Bi, Cu, Se, and O atoms are represented with purple, dark-blue, light-green, and red spheres, respectively.

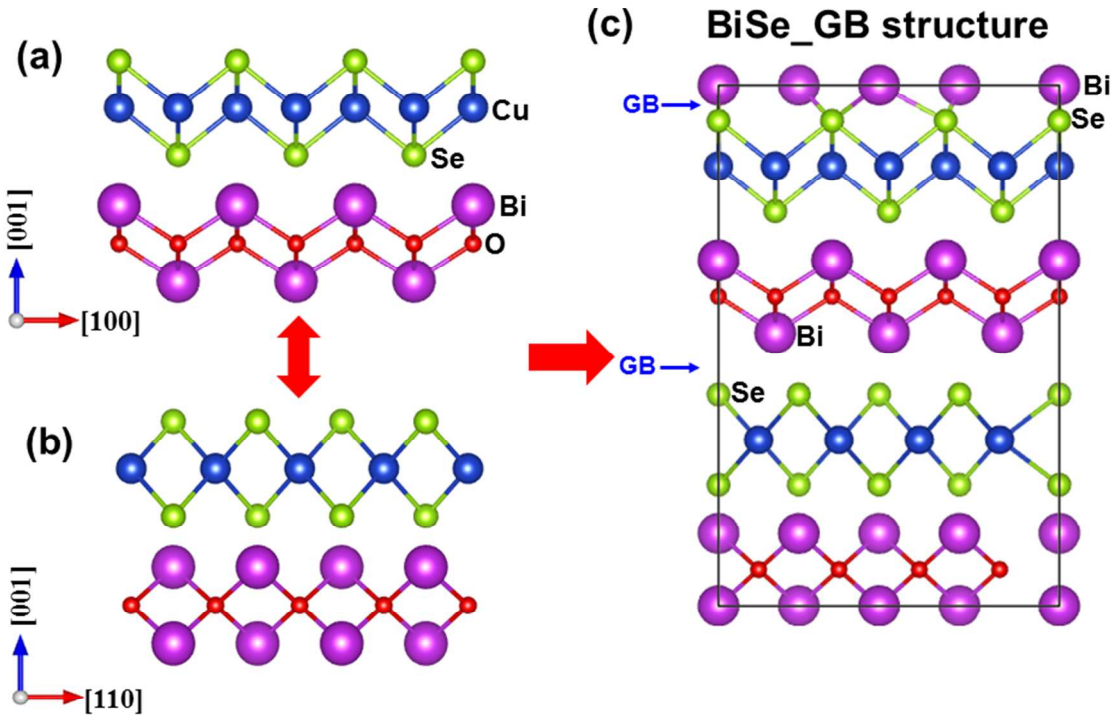

Figure S3. The BiSe_GB structure. The BiCuSeO(100) grain with the Bi atom in the bottom (Figure S3(a)) coheres with the BiCuSeO(110) grain with the Se atom in the top (Figure S3(b)), which forms the BiCuSeO(100) / BiCuSeO(110) GB (Figure S3(c)). Here, the GB structure couples with the Bi-Se bond. Thus, we name this GB as the BiSe_GB. The supercell in Figure S3 (a) contains (3×3×1) BiCuSeO(100) oriented unit cell with the lattice parameter $a = b = 11.85$ Å, $c = 9.09$ Å. The supercell in Figure S3 (b) contains (2×2×1) BiCuSeO(110) oriented unit cell with the lattice parameter $a = b = 11.18$ Å, $c = 9.09$ Å. The CuSe_GB structure contains 136 atoms. The Bi, Cu, Se, and O atoms are represented with purple, dark-blue, light-green, and red spheres, respectively.

Cohering BiCuSeO(100) and BiCuSeO(110) grains in the *a-b* plane

Along the lateral (*a-b*) directions, we theoretically consider several possible coherent structures for each GB, as displayed in Figures S4. Along the *c* axis direction, we roughly estimate an initial bonding distance between the BiCuSeO(100) and BiCuSeO(110) grains for each GB, as shown in Figure S1-S3. All the GB structures are fully relaxed to rearrange the interfacial atoms using the convergence setup as explained in the Methodology section. After relaxation, we calculated the interfacial formation energies for all possible GB structures, as listed in Table 1, and the favorable GB with the lowest formation energy is chosen to study the role of the GB on mechanical properties of the oxide BiCuSeO.

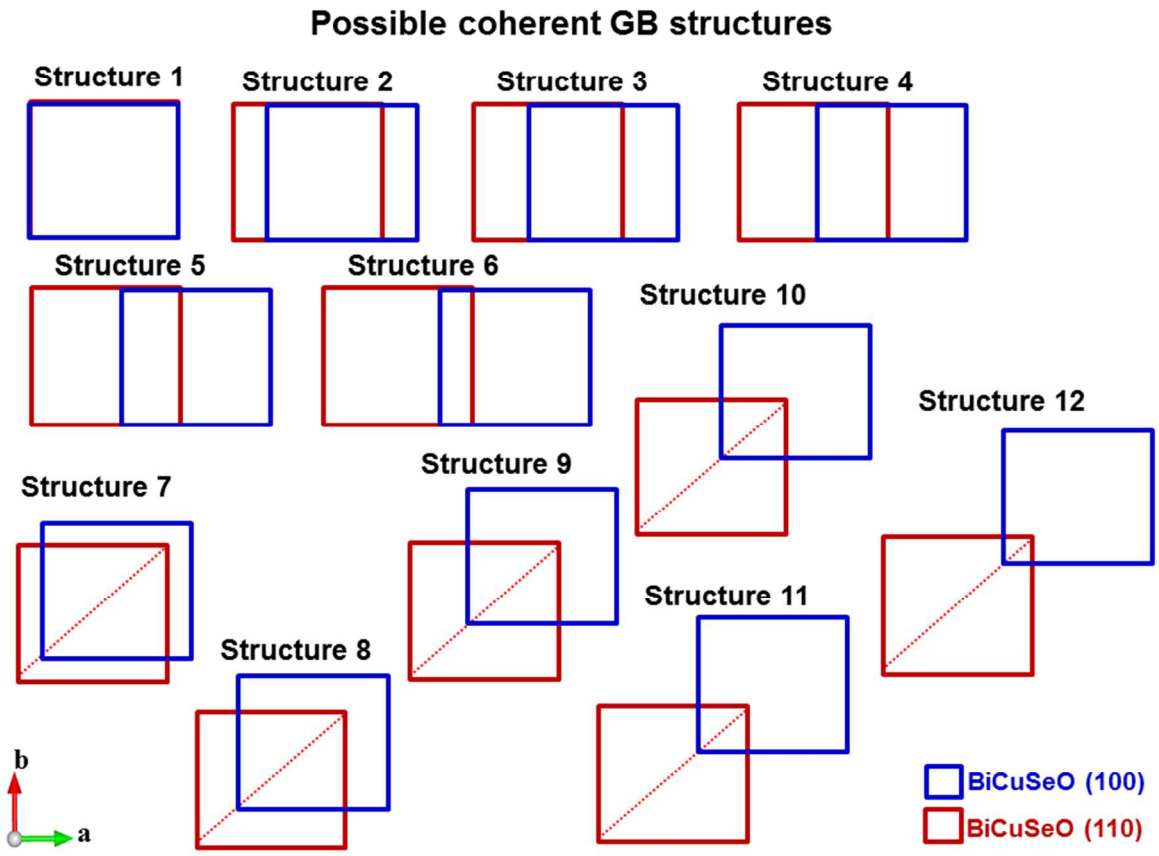

Figure S4. Considered possible coherent structures for the BiCuSeO(100)/BiCuSeO(110) GB. The blue and red squares represent the BiCuSeO(100) and BiCuSeO(110) cells, respectively. The Structure 1 represents the BiCuSeO(100) and the BiCuSeO(110) cells cohere together without any offset. The Structures 2-5 represent the BiCuSeO(100) and the BiCuSeO(110) cells cohere together with an *a* axis offset. Structures 6-12 represent the BiCuSeO(100) and the BiCuSeO(110) cells cohere together with a diagonal offset.